

PATENT SPECIFICATION

1,197,902



NO DRAWINGS

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COMPLETE SPECIFICATION

Low Pressure Oxo Process

- We, THE BRITISH PETROLEUM COMPANY LIMITED, of Britannic House, Moor Lane, London, E.C.2, England, a company incorporated in accordance with the Laws of England, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—
- 5 This invention concerns a novel process for hydroformylating olefins to give aldehydes, using a rhodium complex catalyst.
- 10 The oxo process involves reacting an olefin with carbon monoxide and hydrogen using elevated temperature and pressure. The products are aldehydes and/or alcohols. Cobalt compounds, particularly the octacarbonyl are the most commonly used catalysts but a number of other transition metal compounds have been employed.
- 15 British Patent Specification 1,181,806 discloses and claims a catalyst which is a square planar complex of monovalent rhodium containing at least one carboxylate ligand and a process for the hydroformylation of olefins to give aldehydes and/or alcohols using this catalyst. Alcohols could be produced directly under mild conditions without the need for the separate hydrogenation step to convert 20 aldehydes to alcohols which is often necessary.
- 25 It is now believed that the reaction does in fact take place in two stages, an initial rapid conversion to aldehyde followed by a slower hydrogenation step which converts the aldehyde to the corresponding alcohol. Under the conditions described in our earlier application it was impossible to separate these two reactions but it has now been discovered that if the pressure is reduced sufficiently the 30 hydrogenation reaction becomes so slow as virtually to cease and aldehydes are obtained with practically no formation of alcohols. Reduction of the pressure is always desirable as it reduces equipment cost considerably.
- 35 According to one aspect of the present invention there is provided a process for the hydroformylation of olefins to aldehydes which process comprises hydroformylating an olefin with carbon monoxide and hydrogen at elevated temperature and at a pressure less than 200 psig and in the presence of more than 1 mole of a square planar complex of monovalent rhodium containing a carboxylate ligand per 3600 moles of feed. 45
- 40 Preferably the pressure used lies between atmospheric and 100 psig. 50
- 45 Preferably the mole ratio of catalyst to olefin feed lies between 1:3600 and 1:36.
- 50 The preferred carboxylate ligands are those derived from aliphatic carboxylic acids, particularly those with less than 20 carbon atoms per molecule and most particularly acetic acid, propionic acid and the butyric acids. However some other carboxylate ligands such as the phthalate, cinnamate of p-fluoro benzoate can be used. 55
- 55 The catalyst may contain other complexing ligands additional to the carboxylate ligands. Suitable other complexing ligands are molecules containing an atom of a group Vb or VIb element which has a single pair of electrons available for donation, especially nitrogen or oxygen. Suitable nitrogen-donor ligands of this type include monoalkyl- and monoarylamines, e.g. methylamine, ethylamine, *n*-propylamine, and similar dialkyl-, trialkyl-, diaryl- and triarylamines, e.g. dimethylamine, diphenylamine, trimethylamine and triphenylamine; diamines and triamines e.g., ethylenediamine, diethylenetriamine; ammonia, hydroxylamine, and other molecules of the form NX₂, where X is any suitable group, are acceptable ligands. Suitable oxygen donors will be of the form OX₂, e.g., ethers. In addition, ligands having donor atoms such as phosphorus, arsenic, antimony or sulphur may be present. Suitable ligands of this type will include phosphines, arsines, and stibines, thio-

ethers RR'S; and sulfoxides RR'SO. Other suitable ligands include pyridine and substituted pyridines, e.g. α -picoline, 2,2'-dipyridyl, 1,10-phenanthroline. The preferred catalysts have tertiary phosphine ligands such as triethylphosphine, tri-n-propylphosphine, tri-n-butylphosphine and tri-n-octylphosphine.

To assist the stability of the catalyst on recycle a trialkyl phosphine ligand is preferably used and a catalytic quantity of a carboxylic acid may be present. This acid is preferably the one corresponding to the carboxylate ligand of the catalyst, but may be any other acid whose carboxylate ion will form a catalyst suitable for this invention.

Suitable feeds are olefins having between 2 and 20 carbon atoms per molecule and particularly propylene, hexenes and heptenes.

The double bond is preferably terminal, but may be internal.

The feed may be introduced dissolved in an inert solvent or in the feed or recycled product. The solvent may be a saturated or aromatic hydrocarbon. Normal paraffins such as n-hexane, n-heptane and n-octane are suitable. Alcohols such as n-octanol may also be used as solvents.

The hydroformylation is suitably carried out at a temperature between 40°C and 200°C, most preferably between 80° and 110°C.

The hydrogen to carbon monoxide molar ratio in the feed may be between 4:1 and 1:4. The preferred ratio is 1:1.

The preferred catalyst is suitably prepared by contacting a dicarboxylate complex of tetracarbonyl dirhodium with an alkyl phosphine in an inert solvent.

The invention is illustrated but not limited by the following example.

EXAMPLES

Example 1 was performed in a 350 ml stainless steel autoclave using 30 ml of solvent and 15 ml of hexene-1, the pressure being provided by admixed hydrogen and carbon monoxide. The hydrogen to carbon monoxide molar ratio was 2:1.

The catalyst was prepared by bringing together in n-heptane solution tri-n-butyl phosphine and μ -diacetato tetracarbonyl dirhodium in a mole ratio of 2:1.

The products were extracted and analysed. Details of conditions used and products obtained are given below in Table 1.

Catalyst:



Example 2 does not follow the process of the present invention but is provided for comparison. The catalyst was prepared by treating rhodium carbonyl chloride dimer $(\text{Rh}(\text{CO})_2\text{Cl})_2$ with tri-n-butyl phosphine and a 1:1 hydrogen to carbon monoxide ratio was used.

Example 3 was carried out in a similar fashion to example 1. Differences are indicated in table 2 below.

Examples 4—11 were carried out in Fischer-Porter glass pressure vessels equipped with magnetic stirrers and using a 1:1 mole ratio of $\text{H}_2:\text{CO}$.

Example 12 was carried out in a glass ribbed flask equipped with a paddle stirrer. Gas was bubbled through the reaction mixture throughout the run.

In all examples 4—12 the catalyst was prepared by adding the donor ligand to the appropriate μ -dicarboxylate tetracarbonyl dirhodium species as in example 1.

Results and conditions are set out in table 2 below.

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TABLE 1

Catalyst:Olefin molar ratio	Solvent	Pressure psig	Temperature °C	Time h	Olefin Conversion %	Distribution of Olefin-free products: % mole			
						Branched Aldehyde	Normal Aldehyde	Branched Alcohol	Normal Alcohol
1 : 360	n-heptane	80 ± 5	90 ± 1	2	98	2	31	62	trace

TABLE

LOW PRESSURE HYDROFORMYLATION

Hydrogen: Carbon Monoxide molar ratio

Run No.	Catalyst Ligands				Solvent	Feed Olefin	Olefin: Catalyst molar ratio
	L	x	y	A			
2	<i>n</i> -Bu ₃ P	2	1	Cl	<i>n</i> -heptane	hexene-1	303:1
3	<i>n</i> -Bu ₃ P	2	1	PhCH:CHCOO	<i>n</i> -heptane	hexene-1	427:1
4	aniline	1	2	C ₂ H ₅ COO	<i>n</i> -heptane	hexene-1	400:1
5	Ph ₃ P	2	1	p-FC ₆ H ₄ COO	"	"	"
6	p-toluidine	1	2	C ₂ H ₅ COO	"	"	"
7	pyridine	1	2	C ₂ H ₅ COO	"	"	"
8	<i>n</i> -Pr ₃ P	2	1	Me ₂ CHCOO	"	"	"
9	Et ₃ P	2	1	<i>n</i> -C ₃ H ₇ COO	"	"	"
10	<i>n</i> -Bu ₃ P	2	1	C ₂ H ₅ COO	acetone	octene-1	290:1
11	<i>n</i> -Bu ₃ P	2	1	"	<i>n</i> -octanol	hexene-1	370:1
12	<i>n</i> -Bu ₃ P	2	1	"	<i>n</i> -octane	heptene-1	304:1

Example 1 shows that when the pressure is reduced to 80 psig 98% conversion is still obtained in 2 hours with the formation of only 5% of alcohol.

Example 2 shows the lack of activity of a chloride complex even at 250 psig when compared with our carboxylate catalysts at much lower pressure.

Examples 4—9 illustrate the use of a variety of donor ligands and carboxylate ligands at 100 psig while examples 10—12 show that the preferred catalysts are very active right down to atmospheric pressure.

15 WHAT WE CLAIM IS:—

1. A process for the hydroformylation of olefins to aldehydes which process comprises hydroformylating an olefin with carbon monoxide and hydrogen at elevated temperature and at a pressure less than 200 psig and in the presence as catalyst of more than 1 mole of a square planar complex of monovalent rhodium containing a carboxylate ligand per 3600 moles of feed.

2. A process according to claim 1 where the pressure lies between atmospheric and 100 psig.

3. A process according to either of the preceding claims where the mole ratio of catalyst to olefin feed lies between 1:3600 and 1:36.

4. A process according to any of the preceding claims where the carboxylate ligand is derived from an aliphatic carboxylic acid having less than 20 carbon atoms per molecule.

5. A process according to claim 4 where the carboxylic acid is acetic acid, propionic acid or a butyric acid.

6. A process according to any of claims 1 to 3 where the carboxylate ligand is the phthalate, cinnamate or parafluorobenzoate.

7. A process according to any of the preceding claims where the catalyst also contains complexing ligands which are molecules containing an atom of a group Vb or group VIb element which has a single pair of electrons available for donation.

8. A process according to claim 7 where the Vb or VIb element is nitrogen or oxygen.

9. A process according to claim 8 where the ligand is a monoalkylamine, a monoarylamine, a dialkylamine, a trialkylamine, a di-

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— RhL_x(CO)_y A CATALYSTS

2:1 for Run 3, 1 : 1 for remainder

Time h	Temp. °C	Pressure psig	Olefin Conv. % mole	Product Distribution (% mole, olefin free)			
				Hydro- Carbon	Branched Aldehyde	Normal Aldehyde	Alcohols
8	81 ± 1	250	4	nil	25	75	nil
3	85 ± 1	100 ± 20	98	1	29	65	5
4	80 ± 1	100	7	22	25	53	nil
5	81 ± 4	"	82	negl	49	51	nil
5	80 ± 1	"	8	22	37	41	nil
5	81 ± 3	"	5	22	25	53	nil
5	81 ± 4	"	86	2	32	66	nil
3	86 ± 1	"	64	1	37	62	nil
5	80 ± 1	60	96	2	24	74	nil
4.5	80 ± 1	30	80	negl	23	77	nil
4	80 ± 1	atm	38	negl	25	74	nil

arylamine or a triarylamine.

10. A process according to claim 9 where the donor ligands are dimethylamine, di-phenylamine, trimethylamine, triphenylamine, ethylene diamine, diethylenetriamine, ammonia or hydroxylamine.
11. A process according to any of claims 1 to 8 where the catalyst also contains complexing ligands which are ethers.
12. A process according to any of claims 1 to 7 where the catalyst also contains a complexing ligand containing a phosphorus, arsenic, antimony or sulphur donor atoms.
13. A process according to claim 12 where the ligand is a phosphine, arsine or stibine, a thioether or a sulphoxide.
14. A process according to any of claims 1 to 7 where the catalyst also contains pyridine or substituted pyridine ligands.
15. A process according to claim 14 where the ligands are alpha-picoline, 2,2'-dipyridyl, 1,10-phenanthroline.
16. A process according to any of claims 1 to 7 and 13 where the catalyst also contains tertiary phosphine ligands.
17. A process according to claim 16 where the ligands are tri-ethylphosphine, tri-n-butylphosphine or tri-n-octylphosphine.
18. A process according to any of the preceding claims where a catalytic quantity of a carboxylic acid is present in the reaction mixture.
19. A process according to claim 18 where the carboxylic acid is one corresponding to the carboxylate ligand of the catalyst.
20. A process according to any of the preceding claims where the feed is an olefin having between 2 and 20 carbon atoms per molecule.
21. A process according to claim 20 where the olefin is propylene, a hexene or a heptene.
22. A process according to any of the preceding claims where the feed is introduced dissolved in an inert solvent or in the feed or recycled product.
23. A process according to claim 22 where the solvent is a saturated or aromatic hydrocarbon.
24. A process according to claim 23 where the solvent is a normal paraffin.
25. A process according to claim 24 where the solvent is n-hexane, n-heptane or n-octane.

26. A process according to any of the preceding claims where the solvent is an alcohol.
27. A process according to claim 26 where the solvent is n-octanol.
- 5 28. A process according to any of the preceding claims where the hydroformylation is carried out at a temperature between 40°C and 200°C.
29. A process according to claim 28 where the hydroformylation is carried out at a temperature between 80°C and 110°C.
30. A process according to any of the preceding claims where the hydrogen to carbon monoxide molar ratio in the feed is between 4:1 and 1:4.
- 15 31. A process according to claim 30 where the hydrogen to carbon monoxide molar ratio is 1:1.
32. A process as claimed in any of the preceding claims and as described in example 1 or any of examples 3 to 12.
- 20 33. Aldehydes whenever prepared by a process according to the present invention.

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